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RESEARCH MEMORANDUM

PRESSURE LIMITS OF FLAME PROPAGATION OF PURE

HYDROCARBON-AIR MIXTURES AT REDUCED PRESSURE

By Adolph E. Spakowski

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

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2657

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PRESSURE LIMITS OF FLAME PROPAGATION OF PURE HYDROCARBON-AIR MIXTURES

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SUMMARY

The flammability limits of 18 high-boiling hydrocarbons at reduced
pressures were studied in a closed flame tube with hot-wire ignition.
Characteristic two-lobe flammability-limit curves were exhibited by all
the hydrocarbons studied. The minimum pressure limit was not affected
by the molecular weight.

The rich limit, the lean limit, and the flammability range, when
expressed as volume percent fuel, decreased as the number of carbon
atoms increased. However, if the concentration of fuel is expressed as
percent stoichiometric, the lean limit of the n-alkanes and n-alkenes
attains a maximum value near a molecular weight of 75. Likewise the rich
limit of the same two series attains a maximum near a molecular weight
of 100. The flammability range, when expressed as volume percent fuel
in the mixture, correlated with the molecular weight raised to the
-0.70 power. The rich limit correlated with the lean limit raised to
the 0.56 power.

A correlation between the lean limit and the net molar heat of
combustion held for the n-alkane and n-alkene series through the members
containing ten carbon atoms. The heat of combustion of the lean-limit
mixtures was substantially a constant.

INTRODUCTION

In recent research, one approach to the problem of understanding
complex combustion processes in jet engines has been the study of systems
under carefully controlled conditions. The NACA Lewis laboratory has
used this approach in a program to procure data on the fundamental
properties of hydrocarbons which might be related to the performance of
engine combustion chambers. Several phases of this program have already
been published, including preliminary studies on flame speeds (refer-
ences 1 and 2), minimum ignition energies (reference 3), flammability
limits (reference 4), and quenching distances (references 5 and 6).

The research reported herein presents the flammability limits of several high-boiling hydrocarbons as a continuation of data reported in reference 4. Scattered throughout the literature are a variety of flammability-limit data; however, the apparatus and the conditions of the experiments are so varied that correlations are extremely difficult. Coward and Jones compiled the greater part of these data into a single publication (reference 7). An attempt was made at this laboratory to select an apparatus and a set of conditions which would yield a consistent set of reliable flammability limits. A pressure-flammability-limit curve for each of the 18 hydrocarbons investigated was obtained by use of a vertical glass flame tube 2 inches in diameter and 48 inches long, with a hot-wire ignition source at the lower end. The variation of the flammability limits with the number of carbon atoms is presented graphically herein. From the relation between the rich and lean limits an approximate expression was derived by which the rich limit of fuels may be estimated when their lean limit is known. Molecular weight was also related to flammability range (the rich limit minus the lean limit) by an approximate expression.

SYMBOLS

The following symbols are used in this report:

a,b,c,d   constants

h_c net heat of combustion, kcal/mole

k   constant, 10.40

L   lean limit, percent by volume

R   rich limit, percent by volume

R_a flammability range, percent by volume

W   molecular weight

Subscripts:

d   derived

e   experimental

EXPERIMENTAL DETAILS

Apparatus

In this investigation the tube method of determining pressure-flammability limits was selected. The specific apparatus employed, a modification of that used in reference 4, is illustrated in figure 1.

The fuel metering, mixing, and storing apparatus consisted of a 45-liter galvanized-steel storage tank with sealed stirrer A, fuel capsule B, air inlet H, and precision manometer C. These components were mounted within a glass-walled tank containing ethylene glycol, which served as a constant-temperature bath. The bath temperature was thermostatically controlled at preset temperatures from 50° to 110° C $\pm 0.5^\circ$ C. The test section consisted of a closed glass tube 1.85 inches inside diameter and 48 inches long, joined by a spherical glass joint to the ignition section. The flame tube and the ignition section were enclosed by a cylindrical resistance-wound furnace. Three separate windings were calibrated to give a uniform temperature throughout the length of the flame tube. By means of calibration charts any temperature between 25° and 500° C could be preset. The furnace was provided with a longitudinal slit 1/2 inch wide for visual observation of the flames.

The hydrocarbon-air mixtures were ignited by means of a hot wire, which consisted of about 14 inches of 26-gage Nichrome wire wound in the form of a small helix. The electrical power to the coil was 90 ± 2 watts throughout the investigation (reference 4).

Preparation of Hydrocarbon-Air Mixtures

The hydrocarbons used for this study were either prepared or purified by the Lewis laboratory or by the National Bureau of Standards, and all hydrocarbons had a purity of at least 99 mole percent.

In the preparation of a fuel-air mixture, the fuel-mixture storage tank was first evacuated. Hydrocarbon vapors were then expanded into the system from the fuel capsule (see fig. 1). The partial pressure of the fuel was read on the precision manometer by means of a cathetometer accurate to ± 0.05 millimeter. Air was passed through Anhydrone to remove water and through Ascarite to remove carbon dioxide and then admitted to the system to form the desired fuel-air mixture as calculated on the basis of the ideal gas law. To ensure homogeneity, the mixture was then stirred by a vaned-type stirrer sealed into the tank. After a fuel-air mixture had been prepared, leaner mixtures could be made from it by successive dilutions with air.

PROCEDURE

The method of determining pressure-flammability limits was essentially the same as that reported in reference 4.

For a given fuel-air mixture, propagation was attempted in the flame tube at various pressures until the lowest pressure that would support flame travel was found. The limit was the average between two pressures 2 millimeters apart, only one of which would support flame travel. Flammability was considered in all cases to exist only if the flame traveled the entire length of the flame tube. The limits were all rechecked with the same mixture to ensure reproducibility, which was ±1 millimeter of mercury.

A given pressure-limit curve obtained by measuring the limits for a series of mixtures could be reproduced on subsequent days with fresh mixtures of fuel and air. The results of the check runs are shown as tailed points on the pressure-concentration-limit curves presented herein.

RESULTS AND DISCUSSION

The original data obtained during the course of this investigation are presented as the pressure-flammability-limit curves in figure 2. These curves show the pressure limit plotted against the fuel concentration in the mixture, expressed as percent stoichiometric. Any fuel concentration above the curves will support combustion, while any fuel concentration below the curves will not. This investigation shows that the limits, represented by the bounding vertical sides of the curves, remain nearly constant from approximately 250 millimeters mercury to atmospheric pressure. The minimum point of the curves is referred to as the minimum pressure limit and is the lowest pressure at which any concentration of the hydrocarbon in air will support combustion. Although this point is a function of the apparatus, ignition source, and temperature, it is a constant for a given set of conditions. The minimum pressure limit appears to be independent of the molecular weight. In the subsequent discussion the limits of the hydrocarbons below a molecular weight of 72 are from reference 4. Curves for all the hydrocarbons studied exhibit a characteristic two-lobe shape, although the juncture of the lobes is not always plotted with a high degree of accuracy.

Since higher than room temperatures were required to ensure complete vaporization of the higher hydrocarbons, the resulting data had to be corrected to a reference point designated as room temperature. Data for four of the seven representative hydrocarbons selected for the temperature study were taken from reference 7; for the three others, from NACA

2657

investigations. The average change of the lean limit, expressed as volume percent fuel in the mixture, for the temperature range involved (25° - 80° C) was less than 0.001 percent per °C. The average change of the rich limit, expressed as volume percent fuel in the mixture, over the same temperature range was 0.004 percent per °C. These temperature corrections were applied to the data for the ensuing discussions.

The temperature of the fuel-air mixture in many cases was different from that of the flame tube, which necessitated an investigation of the time required for the gas to assume the flame-tube temperature. For the temperature differences involved, it was found that the gas required a maximum of several seconds to assume the flame-tube temperature.

When the lean limit, expressed as volume percent of fuel in the mixture, is plotted against the number of carbon atoms in the molecule, it decreases quite regularly as the number of carbon atoms increases (fig. 3). The preceding relation holds true for the n-alkanes and the n-alkenes. The curves at the top of figure 3 show the effect of carbon content on the rich limit. Here again the limit decreases regularly as the number of carbon atoms increases. Since the rich flammability limit is decreasing more rapidly than the lean limit, the over-all effect is a decrease of flammability range as carbon content increases.

The flammability limit of the fuel in the mixture, expressed now as the percent stoichiometric, is plotted against the molecular weight in figure 4. For the n-alkanes the lean limit increases slightly to n-pentane and then decreases to n-decane; for the n-alkenes the lean limit increases to n-hexene and then decreases to n-decene. The rich limit for the n-alkanes increases very rapidly from methane to n-heptane and then decreases sharply to n-decane. Omitting ethylene, the first member of the series, the n-alkene rich limit increases from propylene to n-hexene, then levels off through n-decene. From the curves presented in this figure it is seen that the molecular weight affects the rich limit to a larger extent than it affects the lean limit.

The flammability range, that is the rich limit minus the lean limit, expressed as volume percent fuel in the mixture, is plotted against the molecular weight in figure 5. All the hydrocarbons studied, plus those of reference 4, are included in this plot. The two compounds that deviate considerably are methane and ethylene. Also included in the plot are five gasoline samples. Because of the fair degree of correlation shown in figure 5 between the flammability range and the molecular weight, an expression approximately relating the two properties may be written as follows:

$$R_a = aW^b \tag{1}$$

The constants in equation (1) were evaluated, and the resulting equation

$$R_a = 143 \ W^{-0.70} \tag{2}$$

was then used to calculate the flammability range from the known molecular weights for all the hydrocarbons and the gasoline samples included in this discussion. The results are presented in table I. For all the pure hydrocarbons, methane and ethylene excepted, the average deviation of the experimentally determined flammability range from the mean curve as represented by equation (2) was 0.6 volume percent fuel. This error was equal to an average deviation of 6 percent. For the five gasoline samples listed the agreement was very good. The actual average deviation for the five gasolines in volume percent fuel was 0.19, and the average percent of deviation was 3.4.

The lean limit is plotted in figure 6 against the rich limit, both being expressed as volume percent fuel in the mixture. Included in this plot are all the hydrocarbons previously used in figure 5, as well as the five gasoline samples already mentioned. Although this plot is composed of six different hydrocarbon types, there is relatively good correlation for all except ethylene, which deviates considerably. This relation between the lean and rich limits may be stated by the following expression:

$$R = cL^d \tag{3}$$

The constants in equation (3) were evaluated, and the resulting equation

$$R = 7.1 \ L^{0.56} \tag{4}$$

was used to calculate the rich flammability limits from the experimentally determined lean limits for all the included hydrocarbons. The results are presented in table II. For the pure hydrocarbons, ethylene excepted, the average deviation of the experimentally determined values from the mean curve as represented by equation (4) is 0.5 volume percent fuel, which is equivalent to an average deviation of 6 percent. The figures that are given for the gasolines in table II under the heading L_e are values calculated from the experimentally determined lean limits. The average rich limit for the gasolines, from the experimentally determined lean limits, was found to deviate from the average experimental value by 0.78 volume percent fuel, which equals a percent deviation of 12.3.

Egerton and Powling (reference 8) found a correlation between the lean limit and the net molar heat of combustion of the fuel for the

n-alkane series to octane. This same type of correlation was found in this investigation for the n-alkane and n-alkene series to n-decane and n-decene, respectively. This correlation is presented in figure 7, along with that for the three aromatics studied.

Many investigators (references 9 and 10) in the past have found that the combustion heat available in a limit mixture was substantially a constant. This finding was essentially true in the present investigation. In figure 8 the relation between the molecular weight and the heat of combustion of lean-limit mixtures is graphically presented. The ordinate represents the net heat of combustion available in lean-limit mixtures. The n-alkane and n-alkene series are shown plotted with a smooth curve drawn through the n-alkanes.

In calculating the rich limits from experimentally determined lean limits, the greatest deviations for the gasolines are for the two (A and B) from another laboratory (table II). The lean limits found at that laboratory are generally higher than those found at the Lewis laboratory, which in part accounts for differences in deviation of calculated rich limits. Possible experimental differences were overcome by calculating lean limits from known molecular weights and heats of combustion of the mixtures, as shown in figure 8. For the fuels studied an average lean-limit heat of combustion of 10.40 was found. This value, together with the net heat of combustion per mole of the fuel, was used to calculate the lean limit from the relation

$$Lh_c = k \tag{5}$$

The rich limits were then calculated in the normal manner using the expression $R = 7.1 \ L^{0.56}$. The results of these calculations are listed in table II under L_d. For the five gasolines, an average actual deviation of 0.24 volume percent fuel was found, which is equivalent to an average deviation of 3.9 percent from the experimentally determined rich limits.

SUMMARY OF RESULTS

From a study of the pressure-flammability limits of hydrocarbon-air mixtures, the following results were obtained:

1. All the hydrocarbons studied exhibited characteristic two-lobe pressure-concentration curves. The minimum pressure limit was not affected by the molecular weight.

2. When the concentration was expressed as volume percent fuel in the mixture, it was found that the rich limit, lean limit, and flammability range decreased as the number of carbon atoms in the molecule increased.

3. When the concentration of fuel in the mixture was expressed as the percent stoichiometric, it was found that for n-alkanes and n-alkenes the lean limit increased to n-pentane and n-hexene, respectively, and then decreased to n-decane and n-decene, respectively. The rich limit for n-alkanes increased rapidly to n-heptane and then decreased to n-decane. For the n-alkenes, the rich limit increased rapidly to n-hexene and then remained substantially constant through n-decene.

4. The flammability range, when expressed as volume percent fuel in the mixture, was found to correlate with the molecular weight raised to the -0.70 power. This relation was evaluated for all of the hydrocarbons studied and for several fuels with good agreement.

5. The rich limit was found to correlate with the lean limit raised to the 0.56 power. The predicted values for the rich limit from this relation agreed well with those experimentally obtained.

6. The correlation between the lean limit and the net molar heat of combustion was found to hold for the n-alkane and n-alkene series through the ten hydrocarbon members. It was also shown that the heat of combustion of the lean limit mixtures was substantially a constant.

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    Inflammable Gas-Air Mixtures. Pt. I. Mixtures of Air and One Gas
    at the Ordinary Temperature and Pressure. Jour. Chem. Soc. Trans.
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TABLE I - EVALUATION OF EXPRESSION $R_A = 143\ W^{-0.70}$

	Actual deviation (Fuel, percent by volume)	Deviation (percent)
Average for 31 hydrocarbons[a]	0.6	6
Gasoline A[b]	0	0
Gasoline B[b]	-0.3	-4.5
Gasoline C	-0.1	-2.5
Gasoline D	0.4	7
Gasoline E	-0.15	-2.8
Average for 5 gasolines	0.19	3.4

[a] Except ethylene and methane.
[b] Reference 7, temperature effect unknown.

TABLE II - EVALUATION OF THE EXPRESSION $R = 7.1\ L^{0.56}$

	Actual deviation (Fuel, percent by volume)		Deviation (percent)	
	L_e	L_d	L_e	L_d
Average for 32 hydrocarbons[a]	0.5	----	6.0	----
Gasoline A[b]	1.4	0.0	19.7	0.0
Gasoline B[b]	1.0	0.5	20.8	9.4
Gasoline C	-1.1	-0.3	-14.9	-4.2
Gasoline D	0.1	0.1	1.5	1.5
Gasoline E	0.3	0.3	4.8	4.6
Average for 5 gasolines	0.78	0.24	12.3	3.9

[a] Except ethylene.
[b] Reference 7, temperature effect unknown.

A   Storage tank
B   Fuel capsule
C   Precision manometer
D   Flame tube
E   Pressure gage
F   Ignition coil
G   Resistance-wound furnace
H   Dried-air inlet
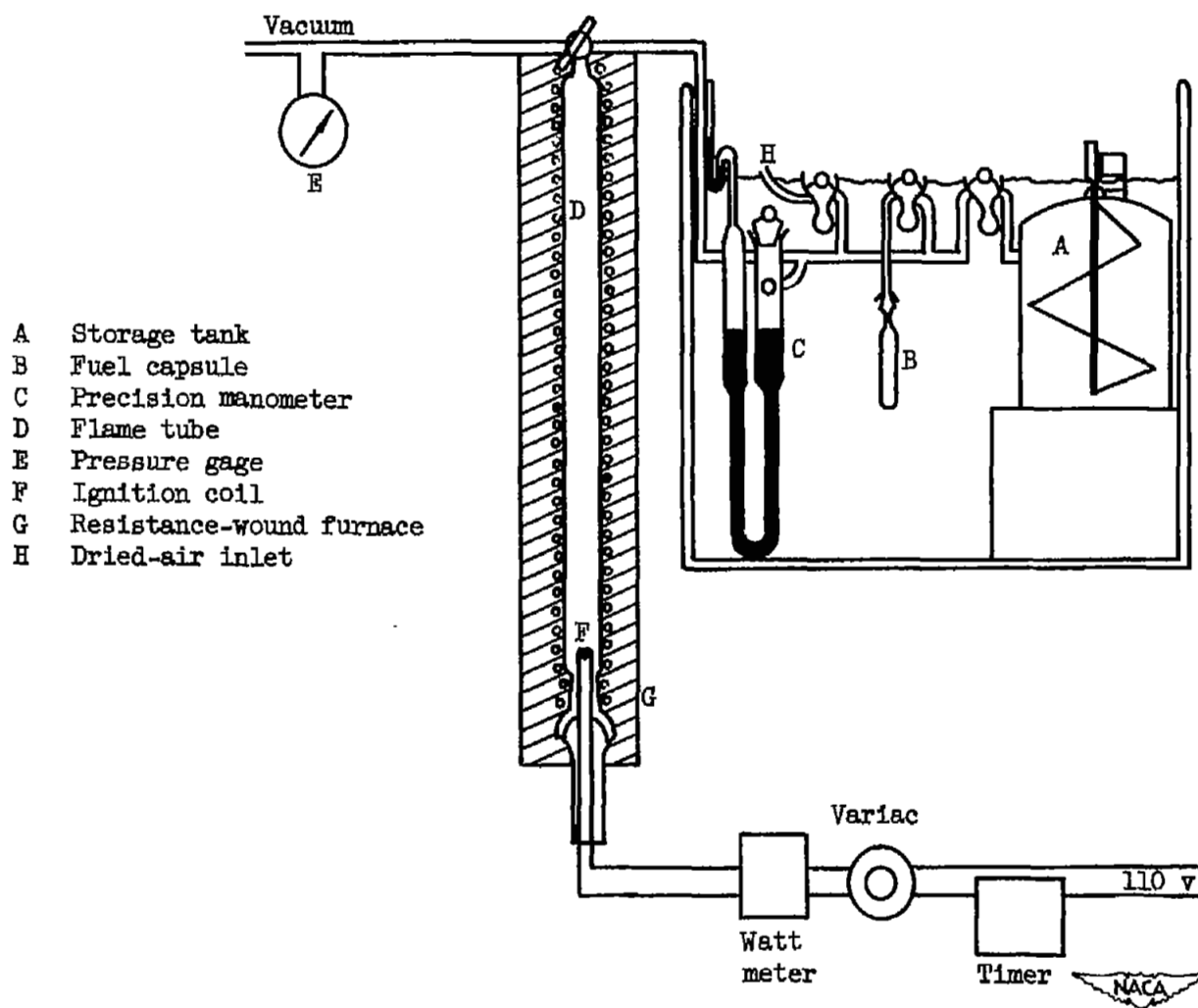
Figure 1. - Apparatus for determining flammability limit.
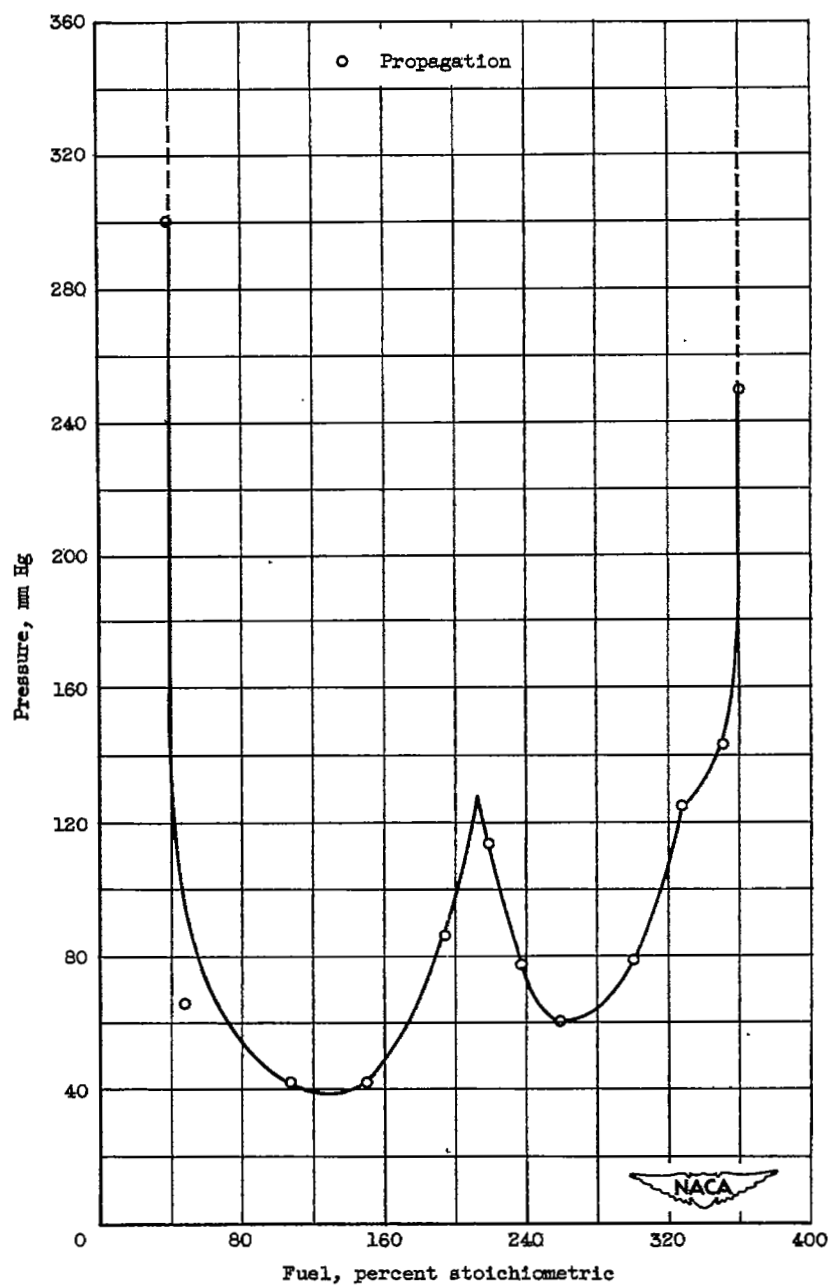
(a) n-Pentane and air. Flame-tube temperature, 28° C.

Figure 2. - Pressure-flammability limits in closed flame tube.
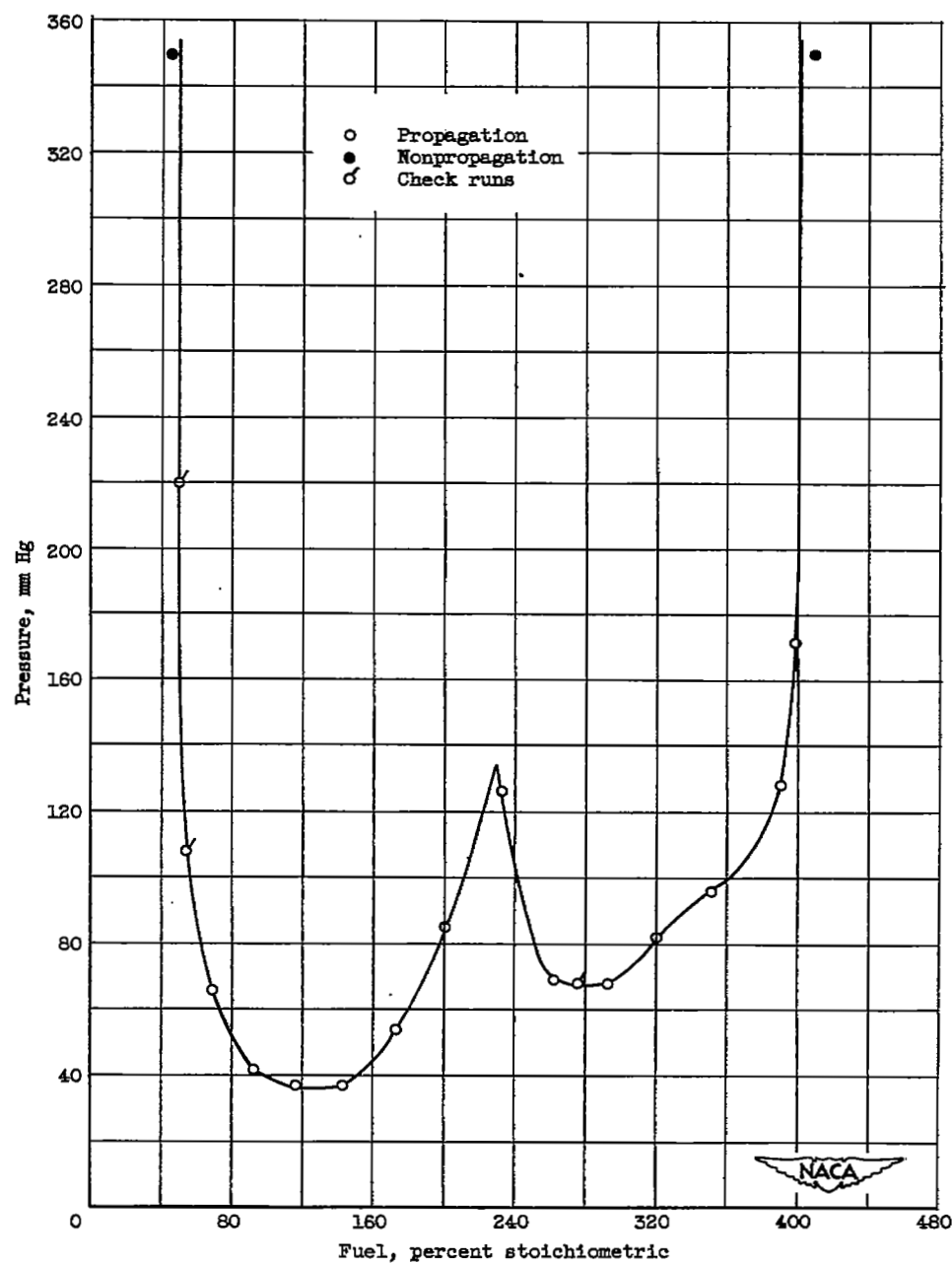
(b) n-Hexane and air. Flame-tube temperature, 50° C.

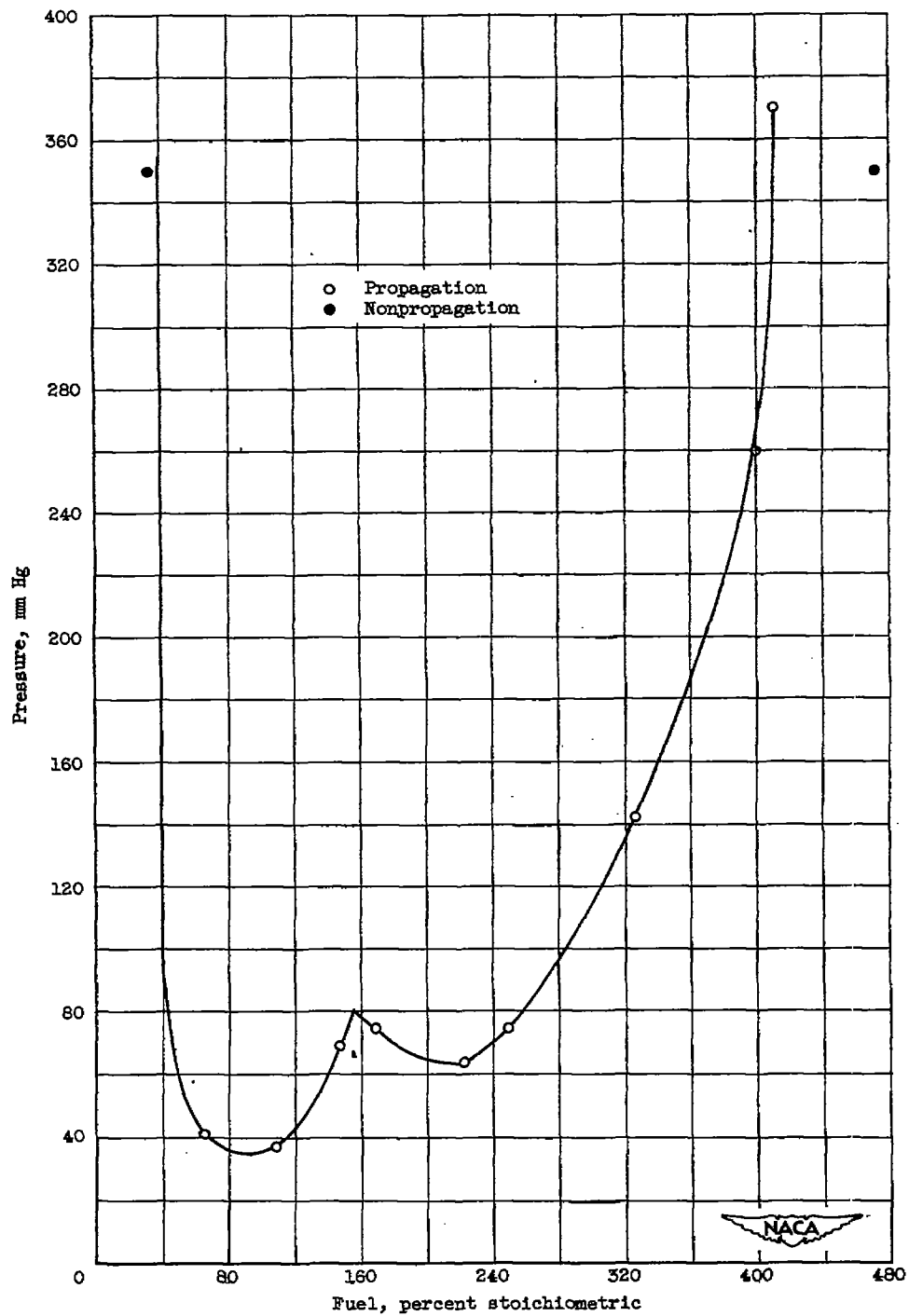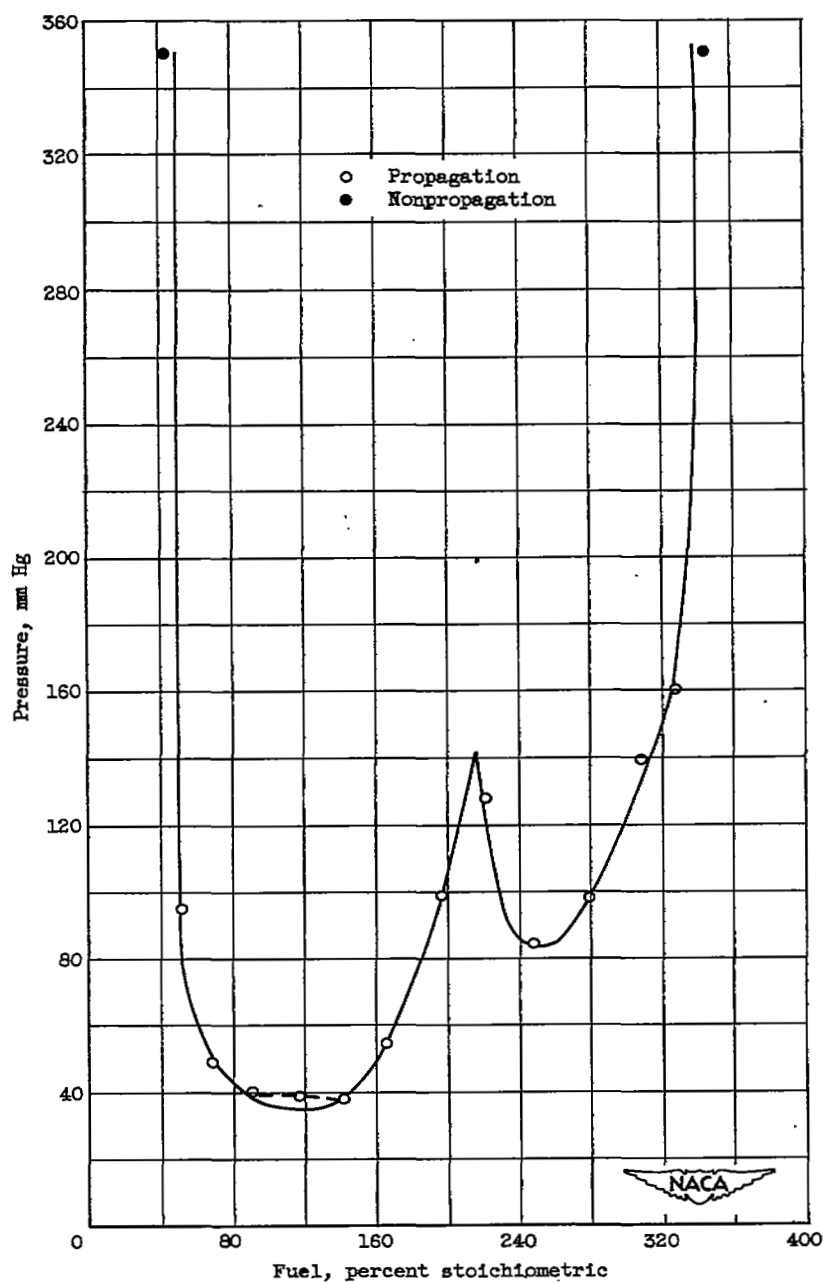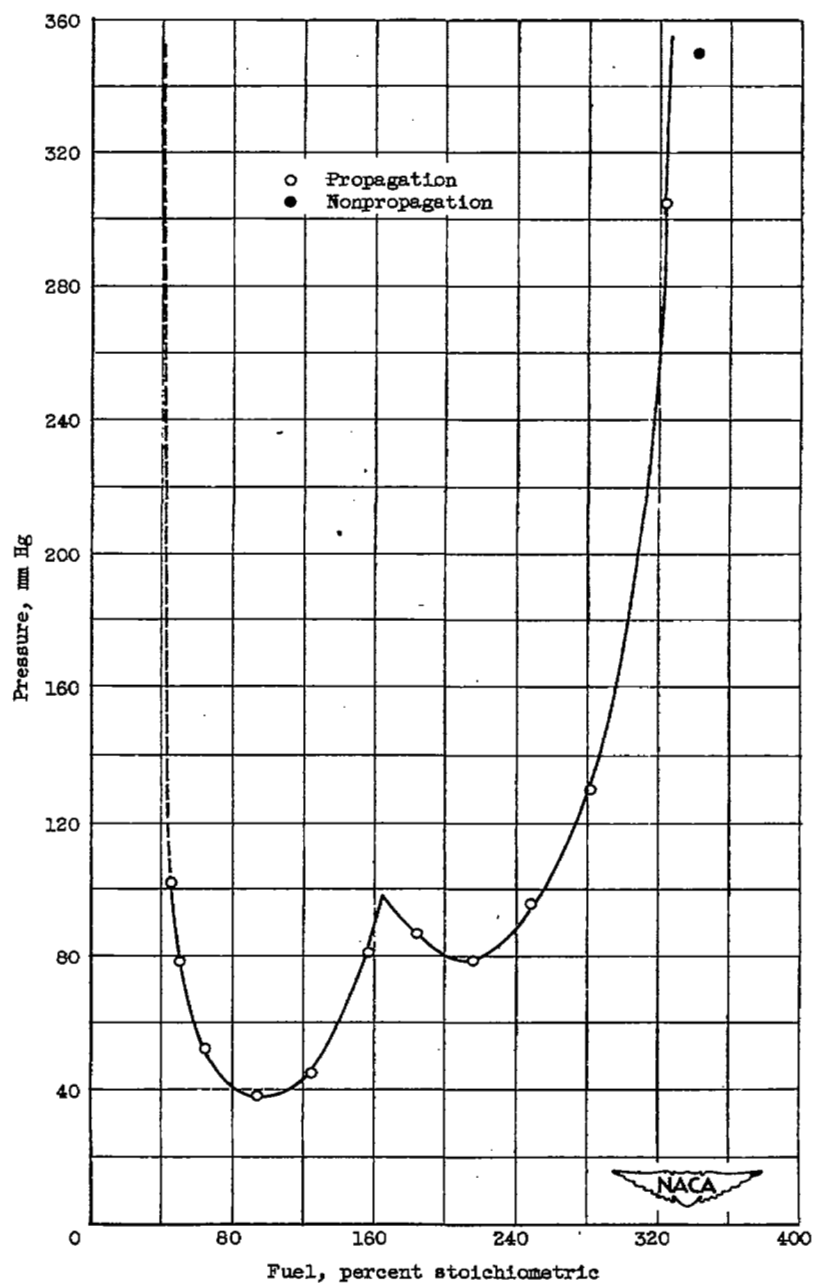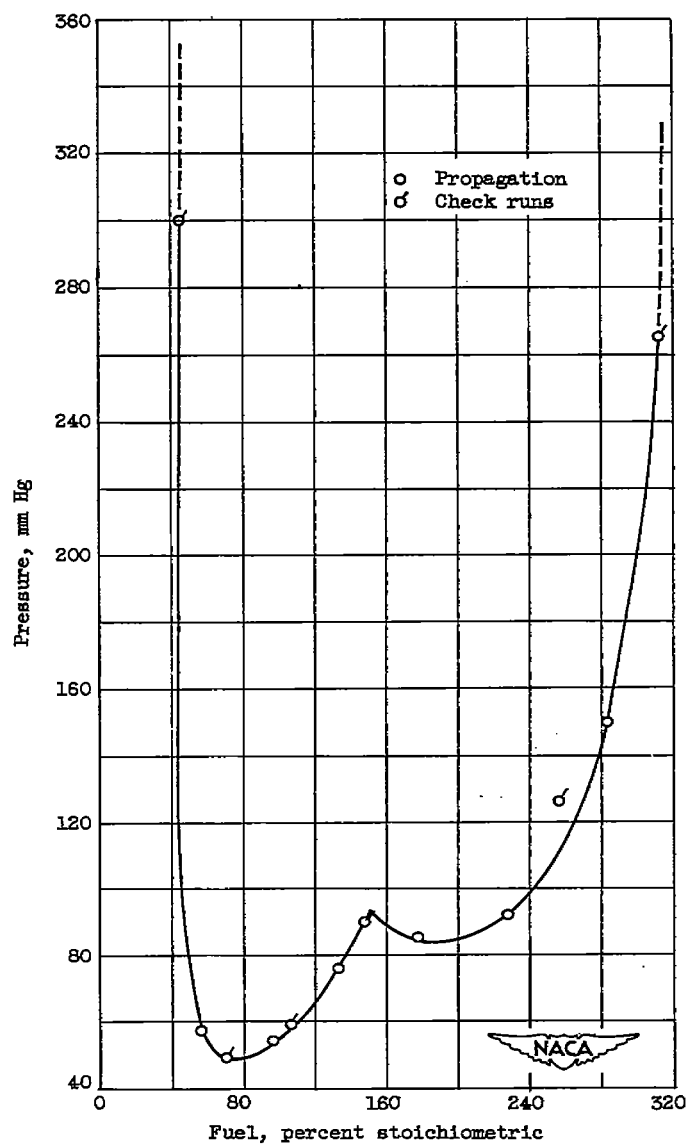Figure 2. - Continued. Pressure-flammability limits in closed flame tube.
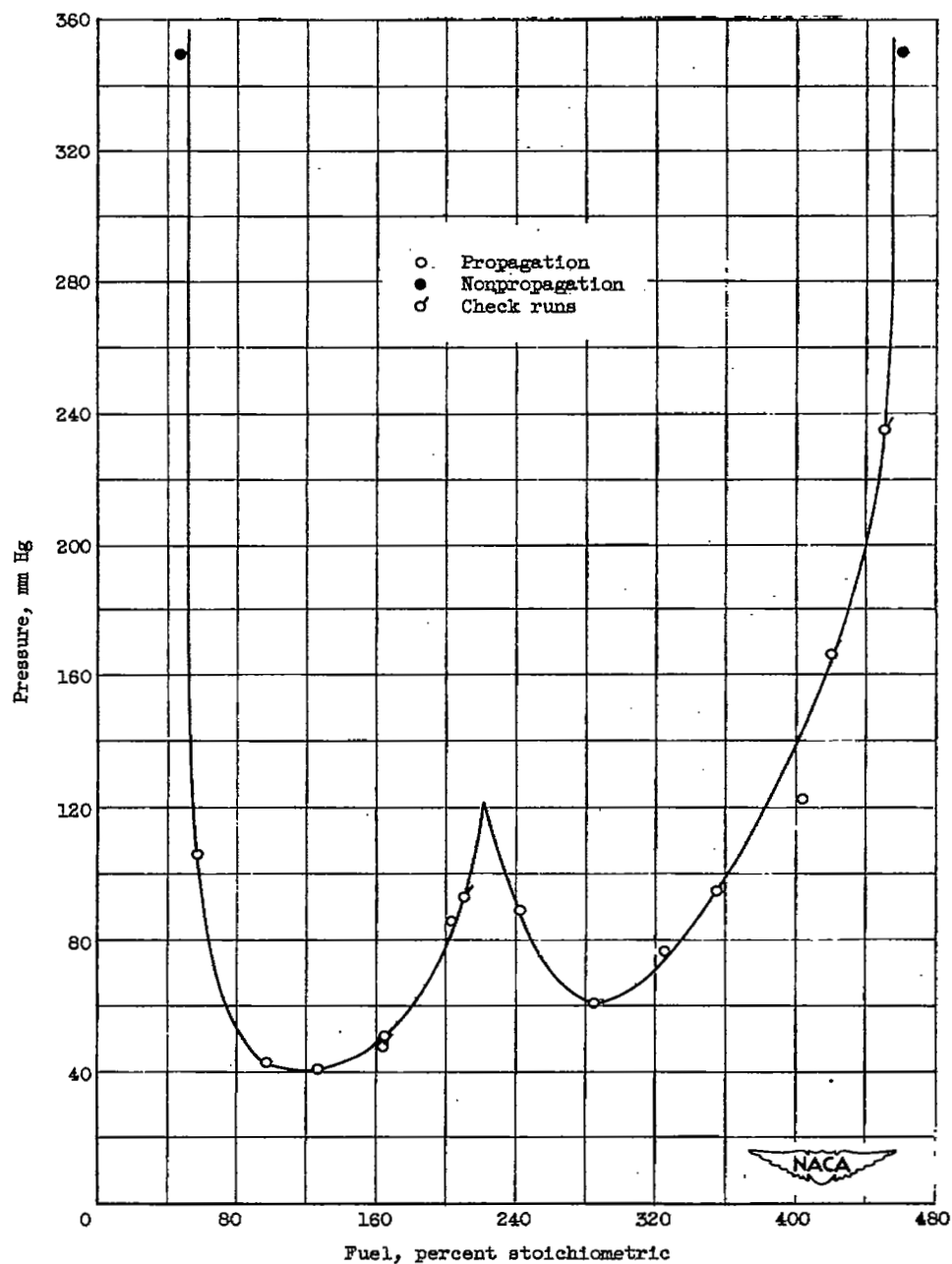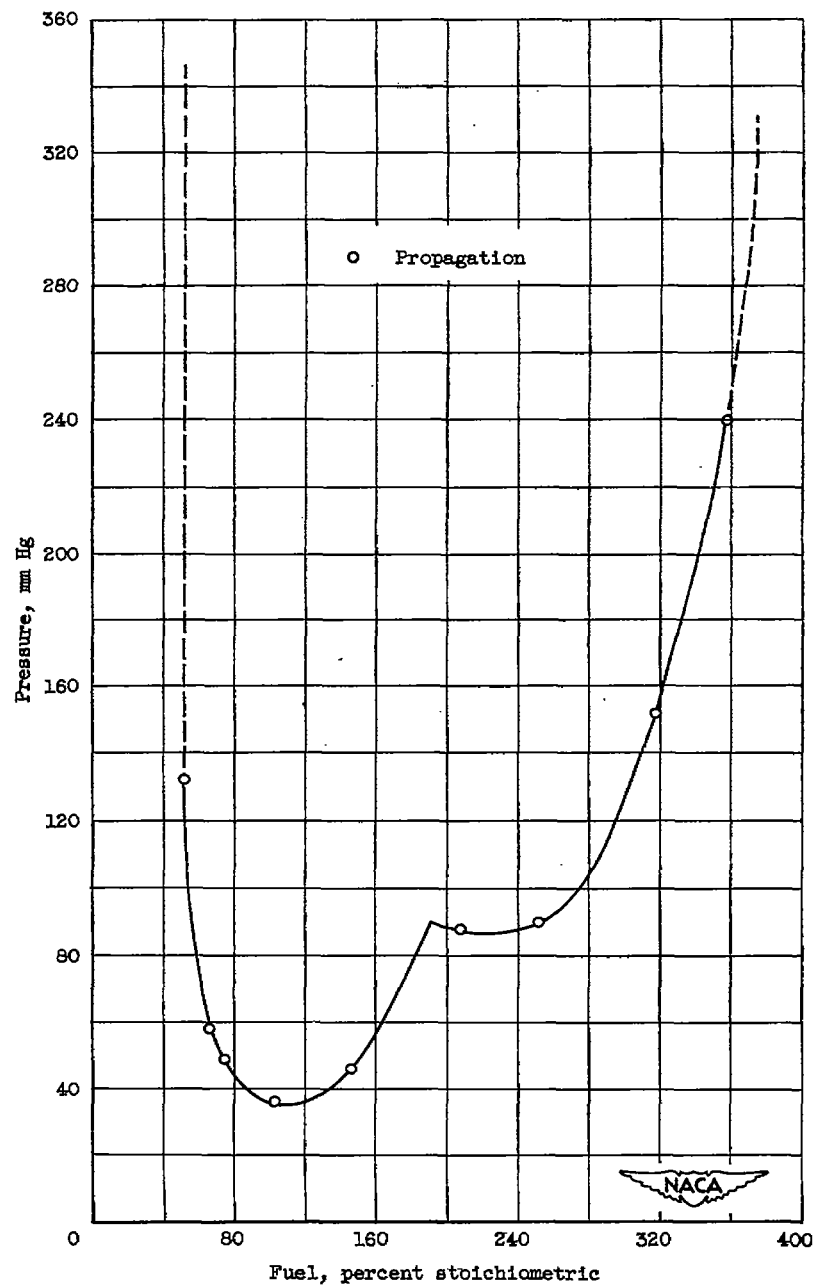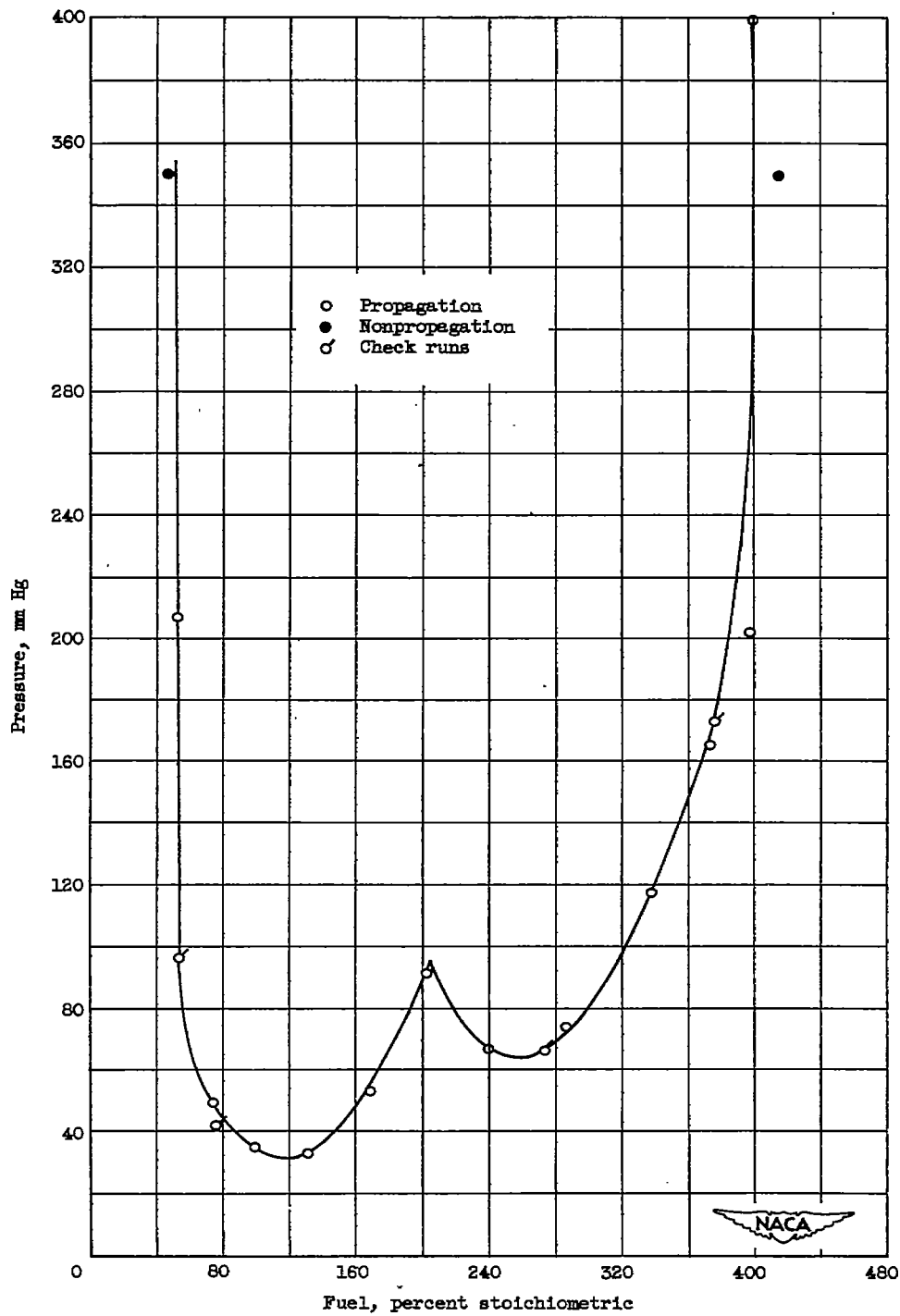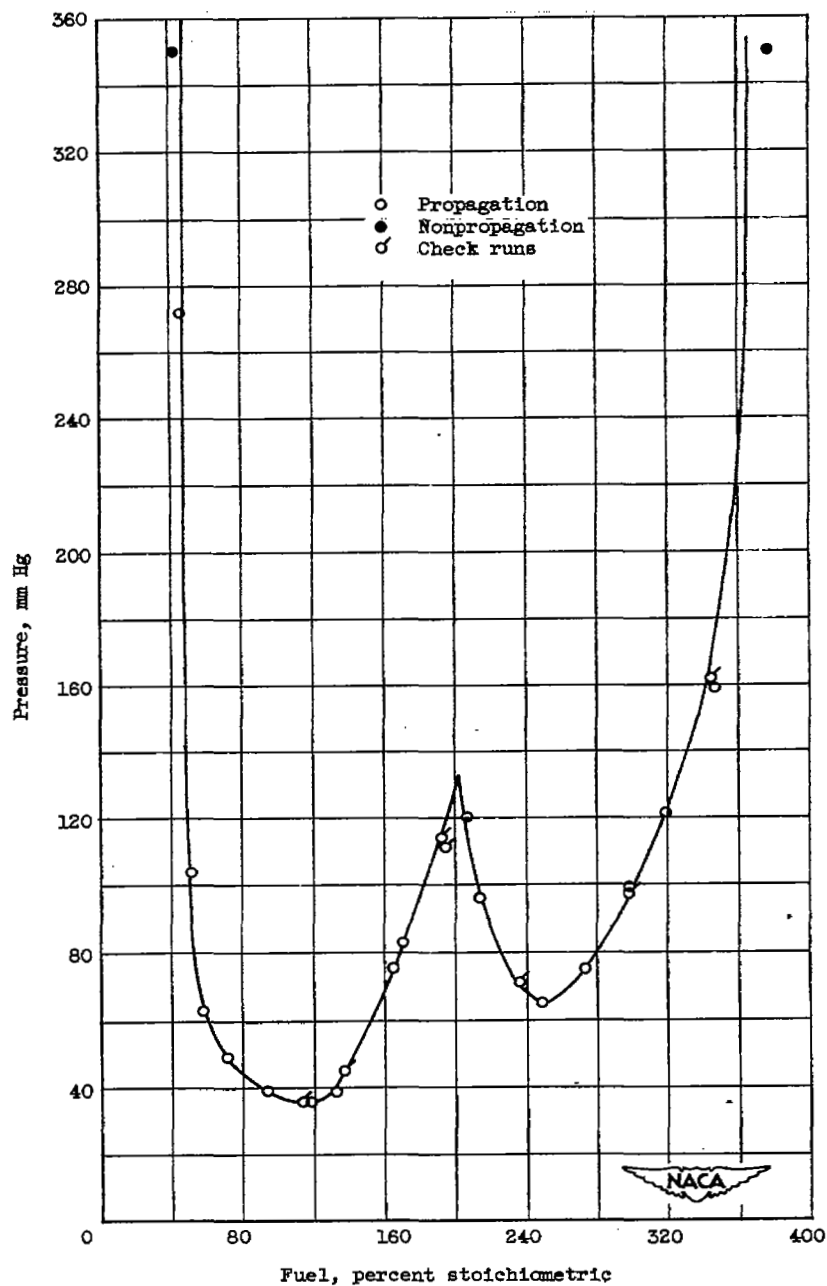
(c) n-Heptane and air. Flame-tube temperature, 50° C.

Figure 2. - Continued. Pressure-flammability limits in closed flame tube.

2657
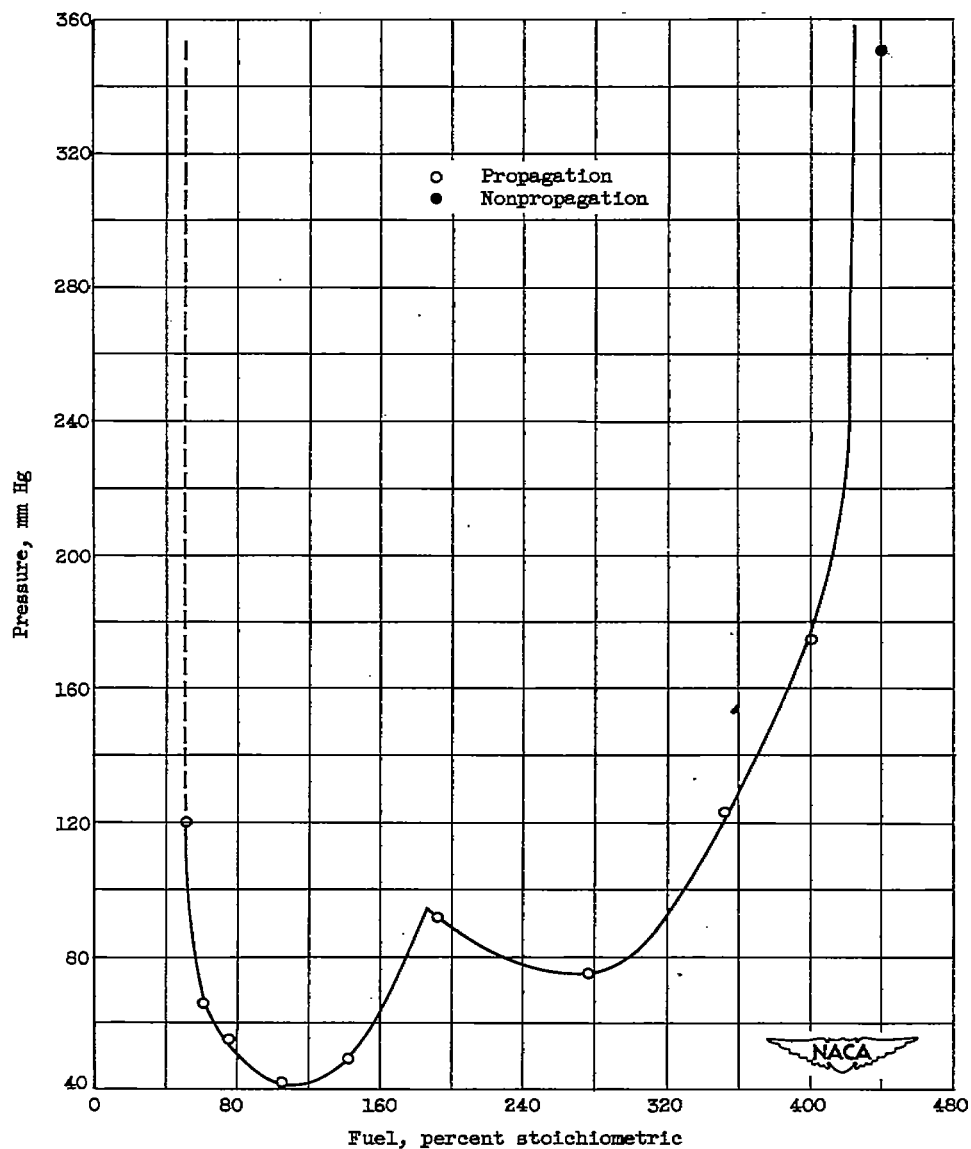
(d) n-Octane and air. Flame-tube temperature, 80° C.

Figure 2. - Continued. Pressure-flammability limits in closed flame tube.
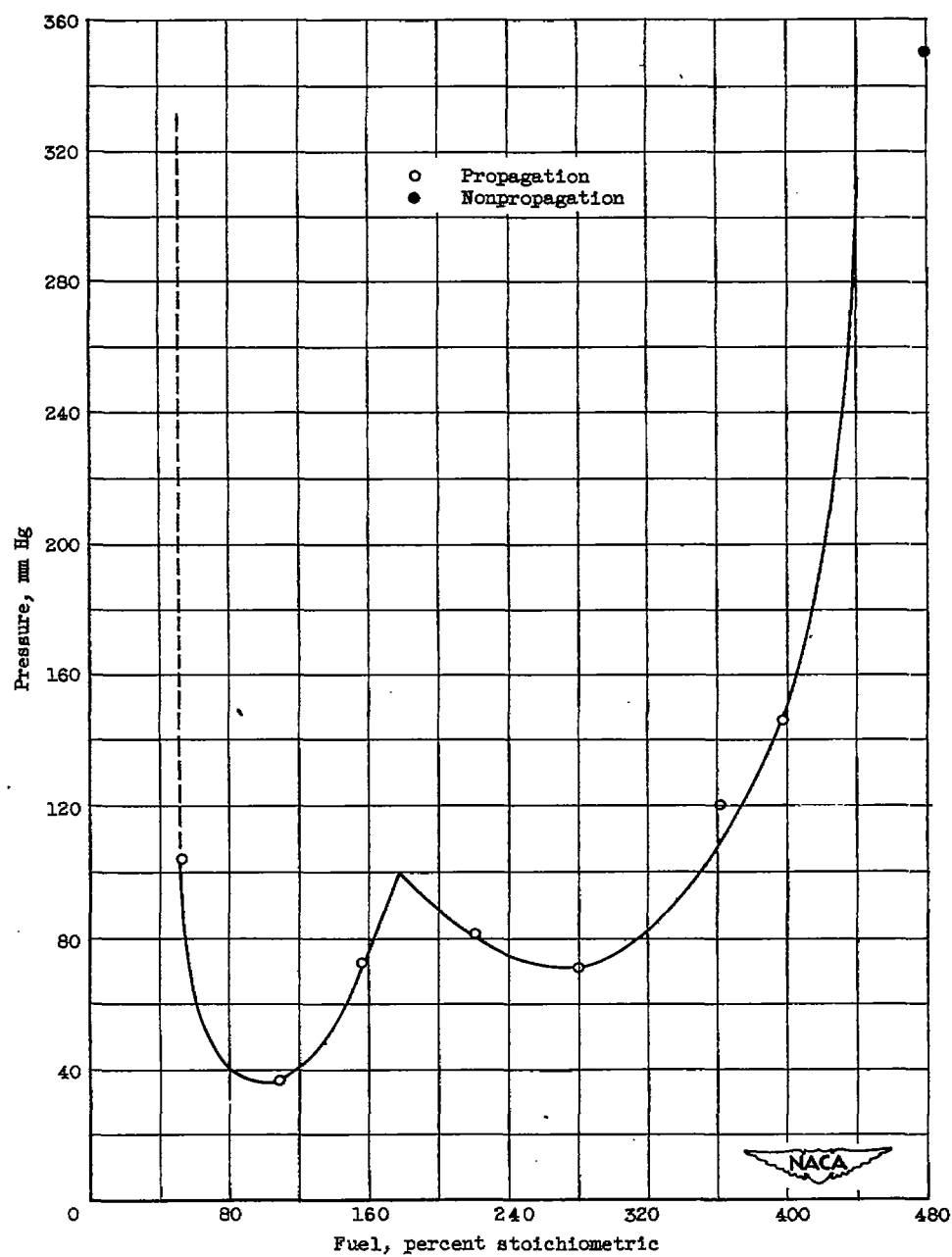
(e) n-Nonane and air. Flame-tube temperature, 80° C.

Figure 2. - Continued. Pressure-flammability limits in closed flame tube.
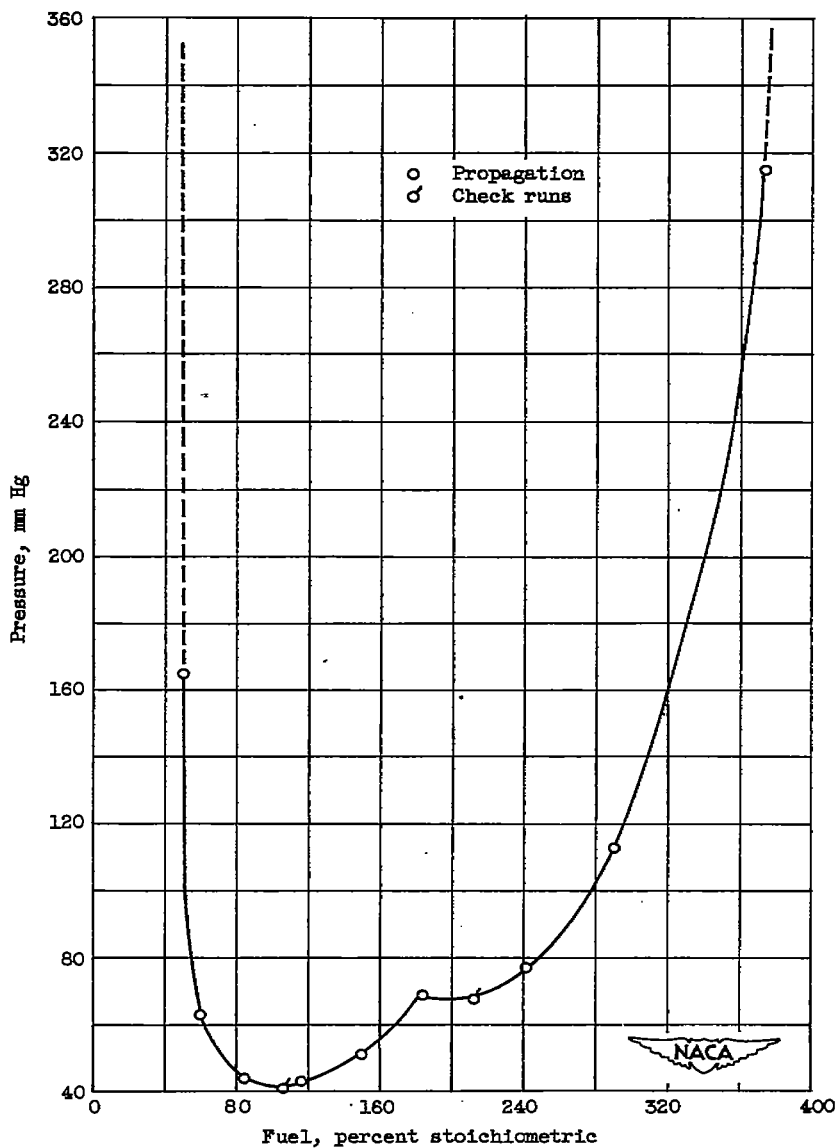
(f) n-Decane and air. Flame-tube temperature, 80° C.

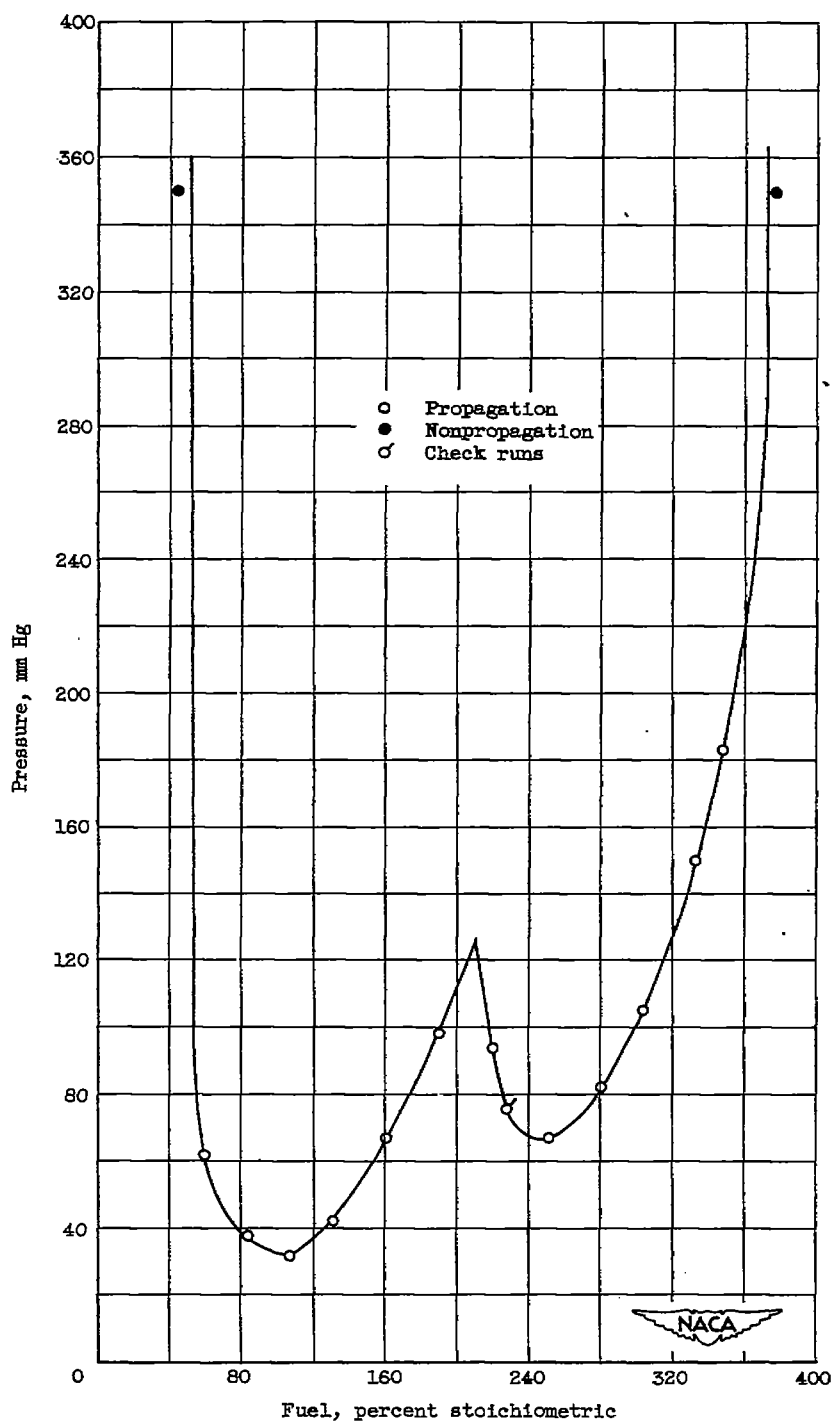Figure 2. - Continued. Pressure-flammability limits in closed
flame tube.
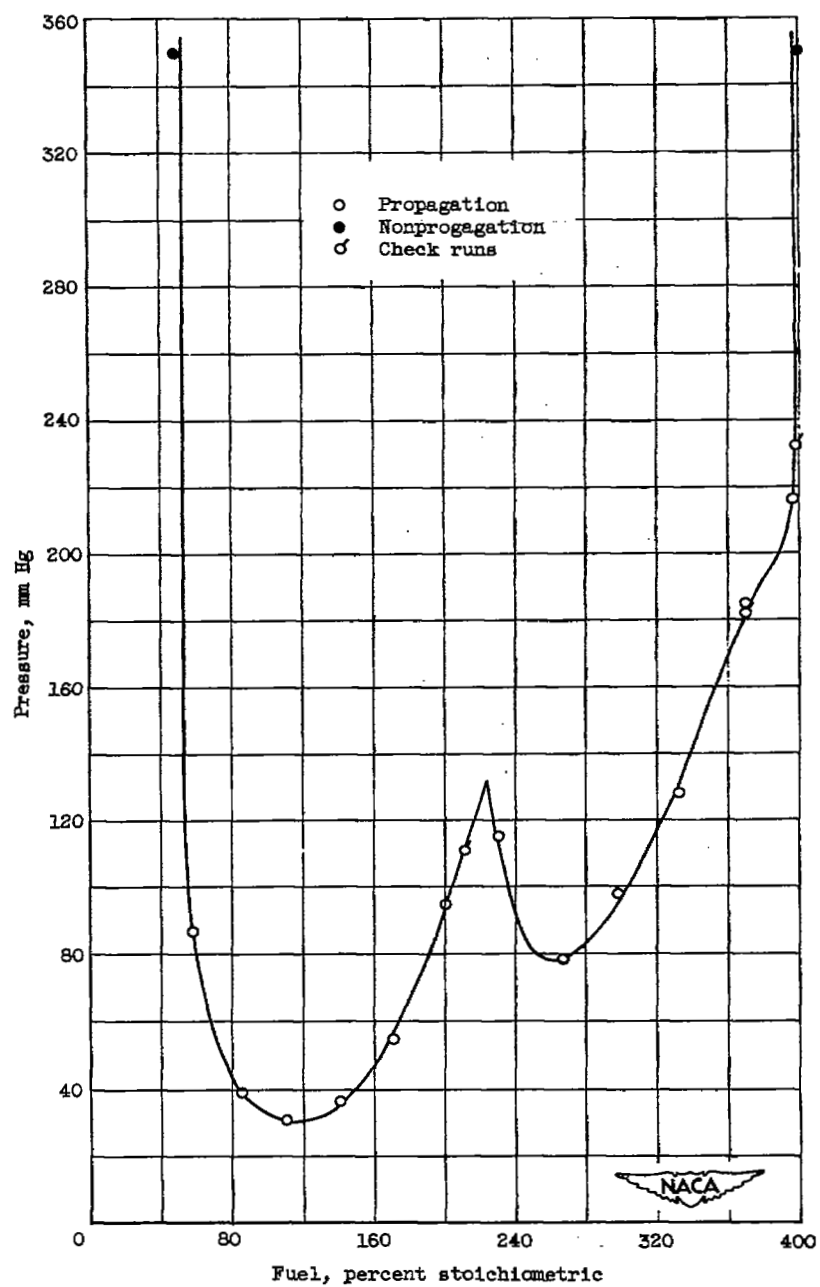
(g) n-Hexene and air. Flame-tube temperature, 50° C.

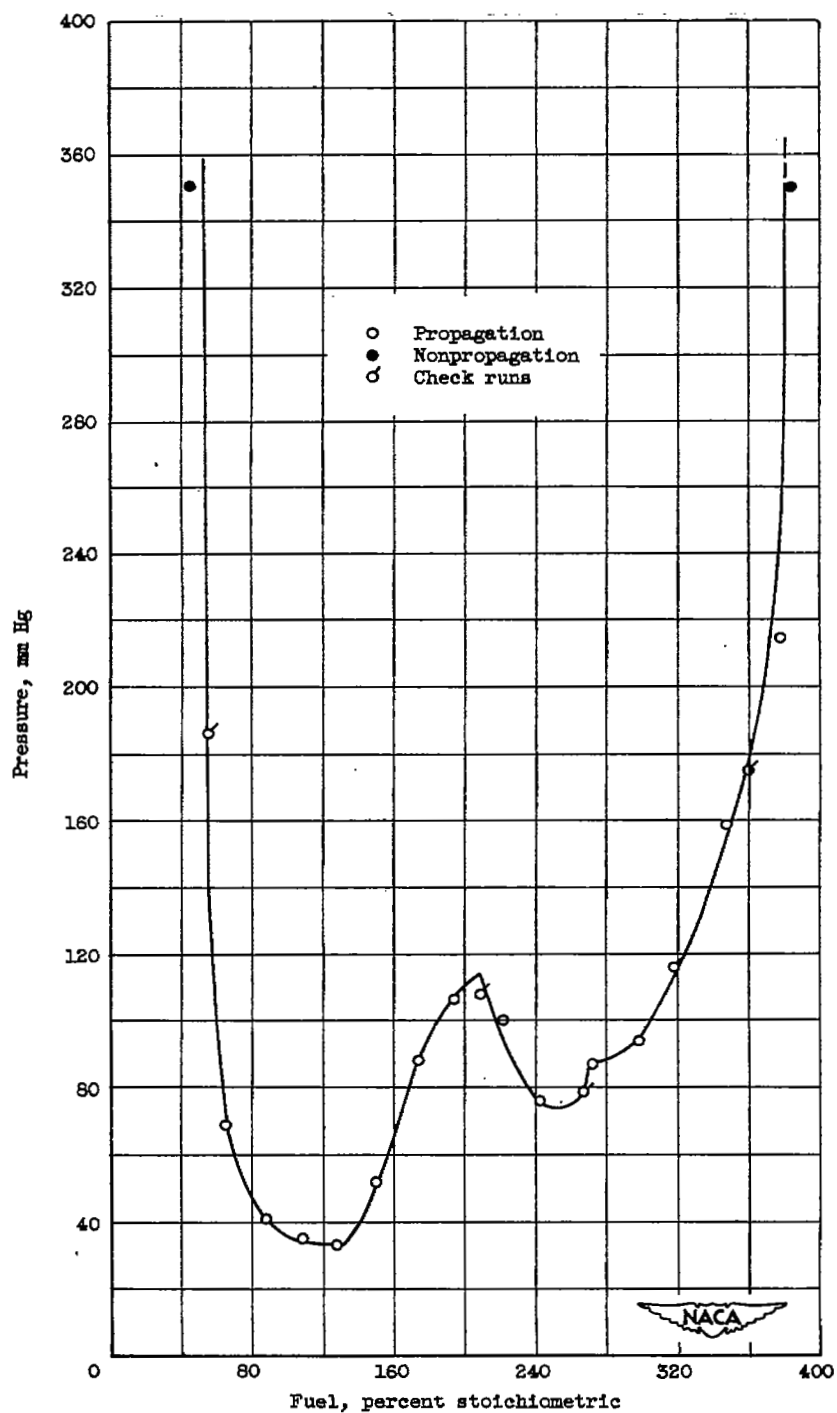Figure 2. - Continued.   Pressure-flammability limits in closed
flame tube.

2657
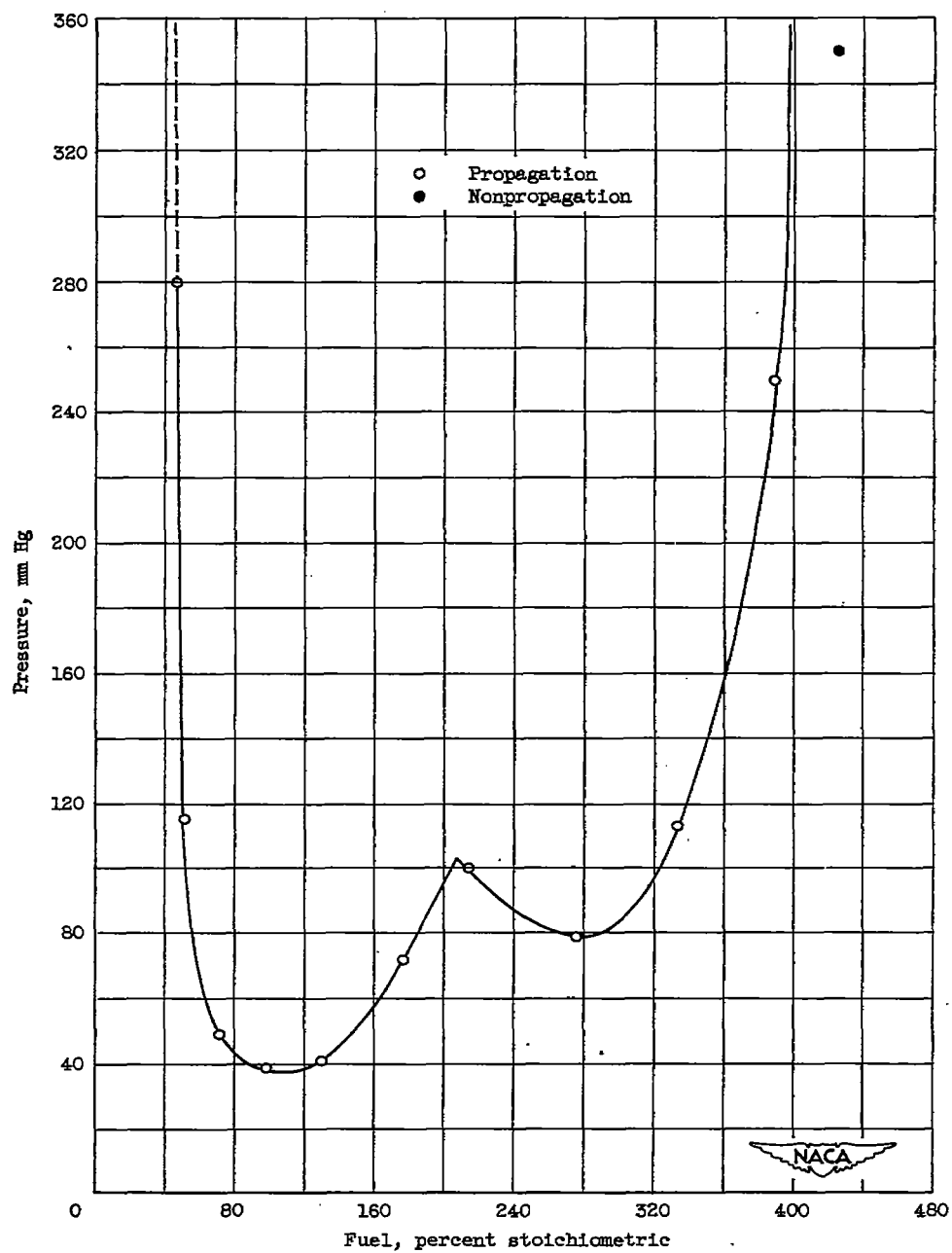
(h) 1-Octene and air. Flame-tube temperature, 80° C.

Figure 2. - Continued. Pressure-flammability limits in closed flame tube.

(i) 1-Decene and air. Flame-tube temperature, 80° C.

Figure 2. - Continued. Pressure-flammability limits in closed flame tube.

(j) Benzene and air. Flame-tube temperature, 50° C.

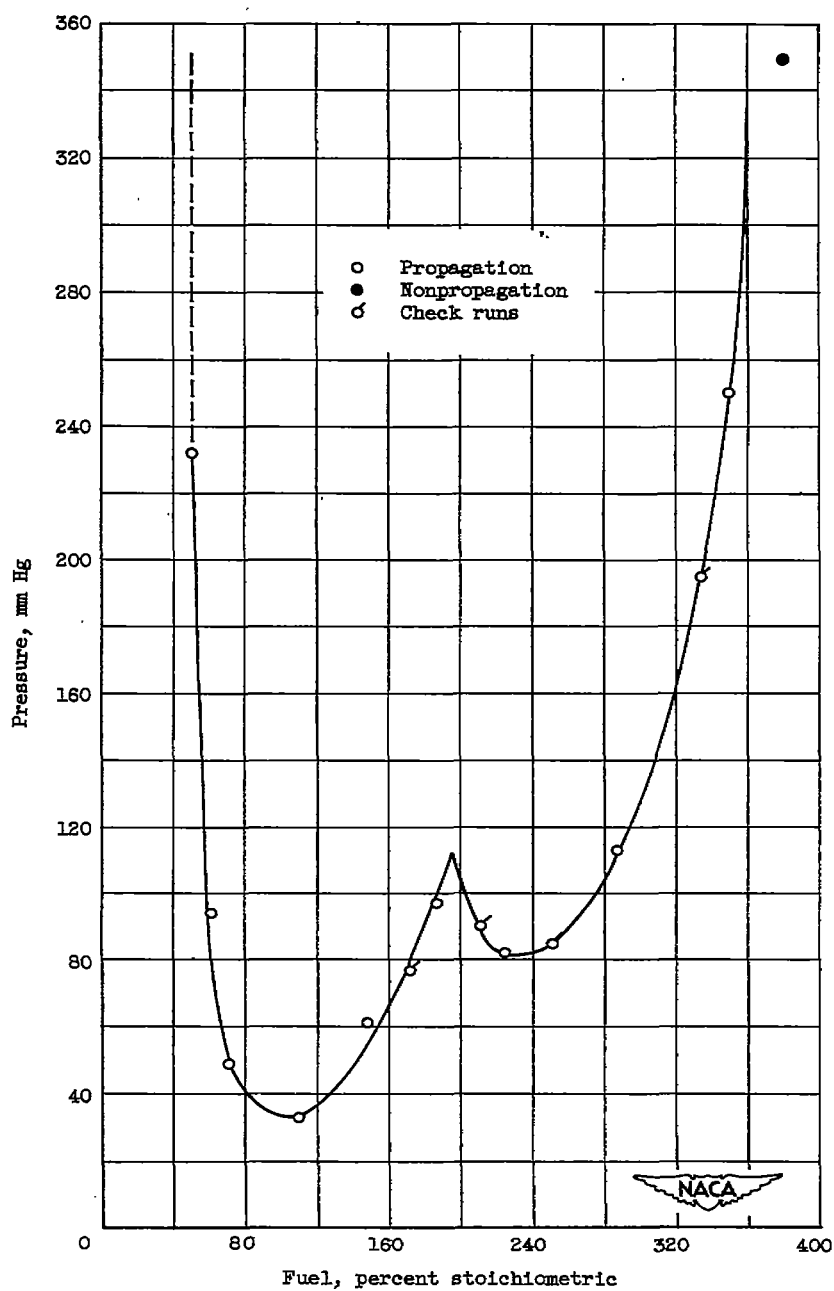Figure 2. - Continued. Pressure-flammability limits in closed flame tube.

(k) Toluene and air. Flame-tube temperature, 50° C.

Figure 2. - Continued. Pressure-flammability limits in closed
flame tube.

(1) m-Xylene and air. Flame-tube temperature, 80° C.

Figure 2. - Continued. Pressure-flammability limits
in closed flame tube.

(m) Isopropylbenzene and air. Flame-tube temperature, 80° C.

Figure 2. - Continued.   Pressure-flammability limits in closed flame tube.

(n) Cyclohexane and air. Flame-tube temperature, 50° C.

Figure 2. - Continued. Pressure-flammability limits in closed flame tube.

(c) Methylcyclohexane and air. Flame-tube temperature, 50° C.

Figure 2. - Continued. Pressure-flammability limits in closed flame tube.

2657

(p) Methylcyclopentane and air. Flame-tube temperature, 50° C.

Figure 2. - Continued. Pressure-flammability limits in closed
flame tube.

(q) Di-isopropyl and air. Flame-tube temperature, 50° C.

Figure 2. - Continued. Pressure-flammability limits in closed
flame tube.

2657

(r) 2,2,4-Trimethylpentane and air. Flame-tube temperature, 50° C.

Figure 2. - Concluded. Pressure-flammability limits in closed
flame tube.
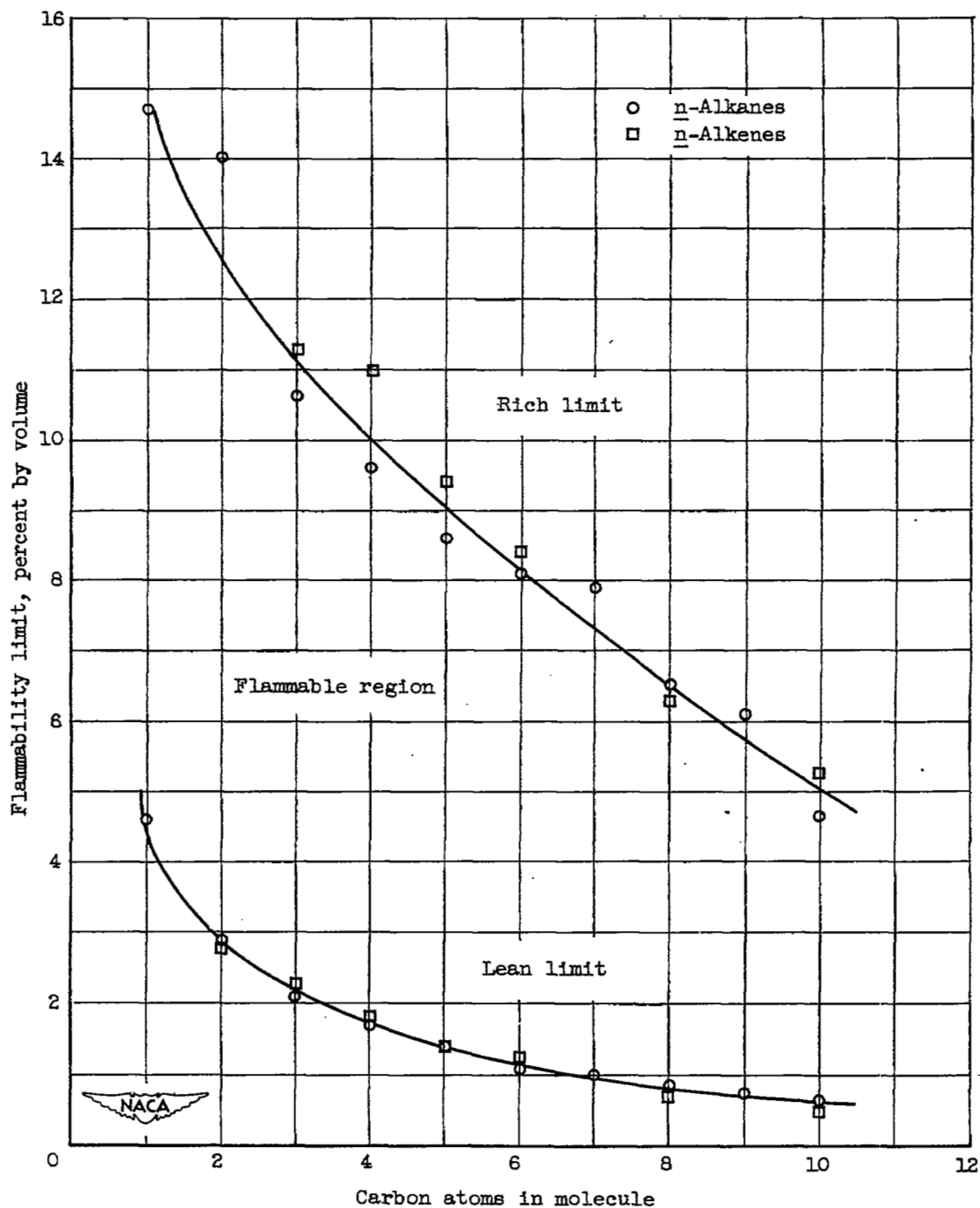
Figure 3. - Effect of number of carbon atoms on flammability limits.

2657
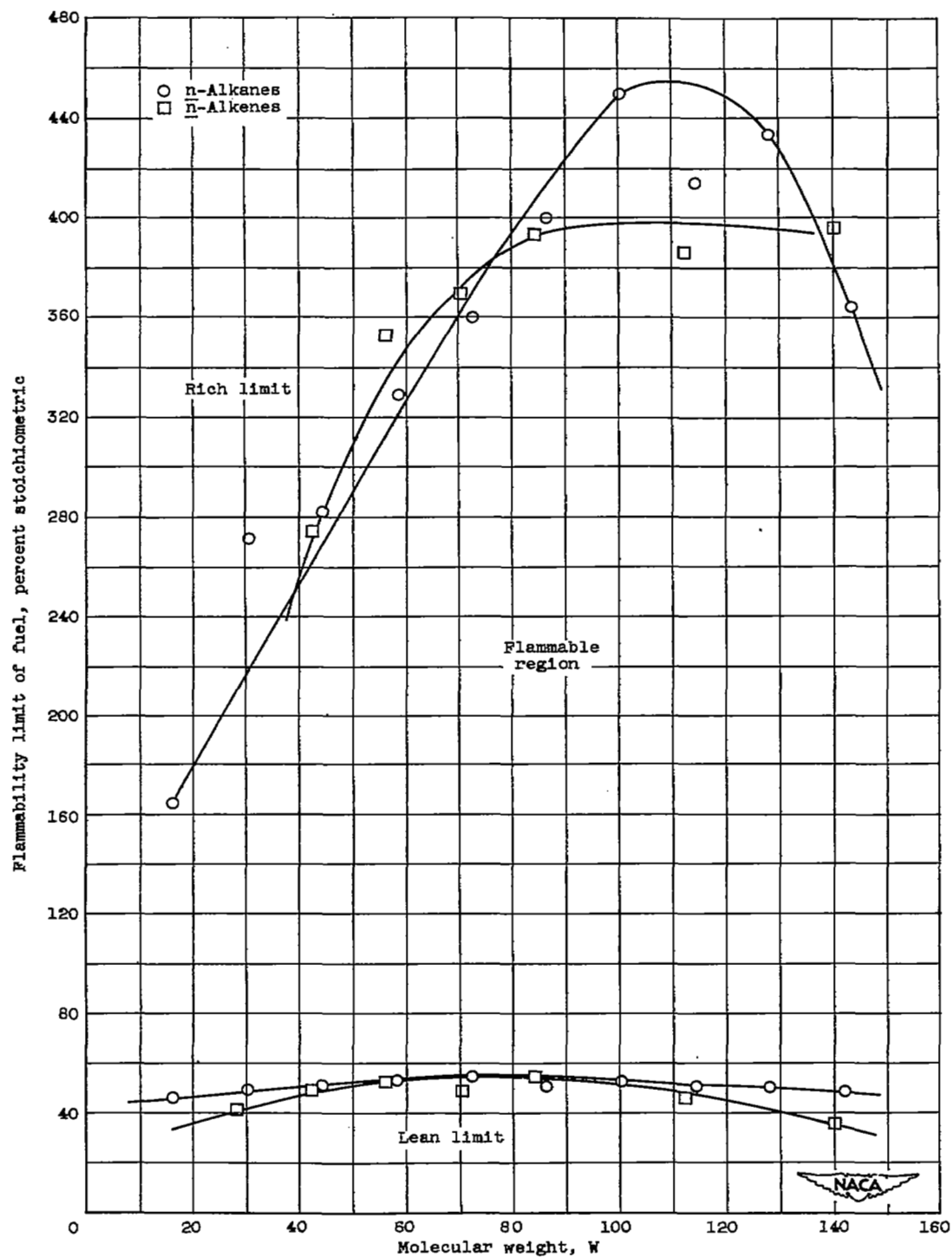
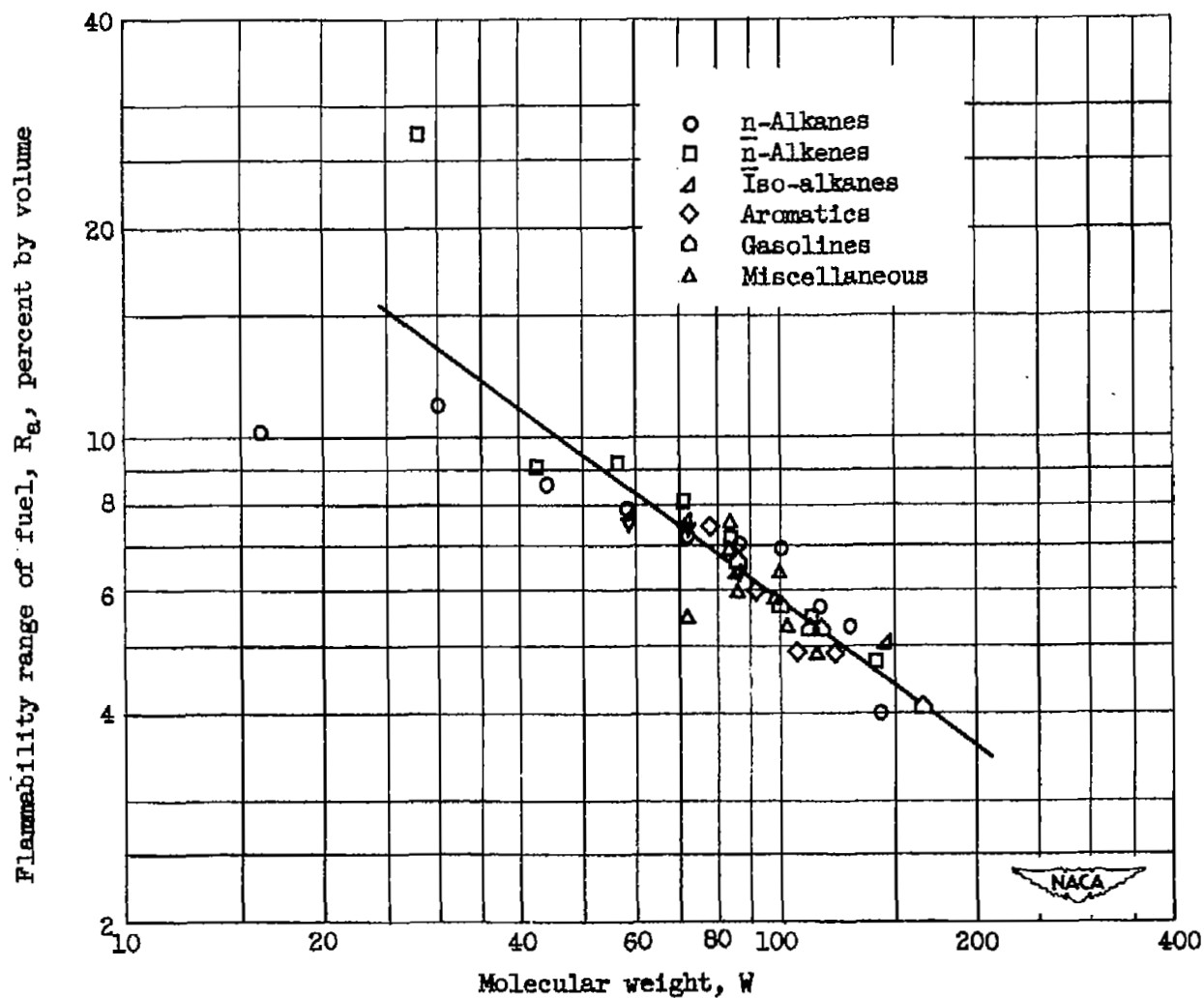Figure 4. - Effect of molecular weight on flammability limits.

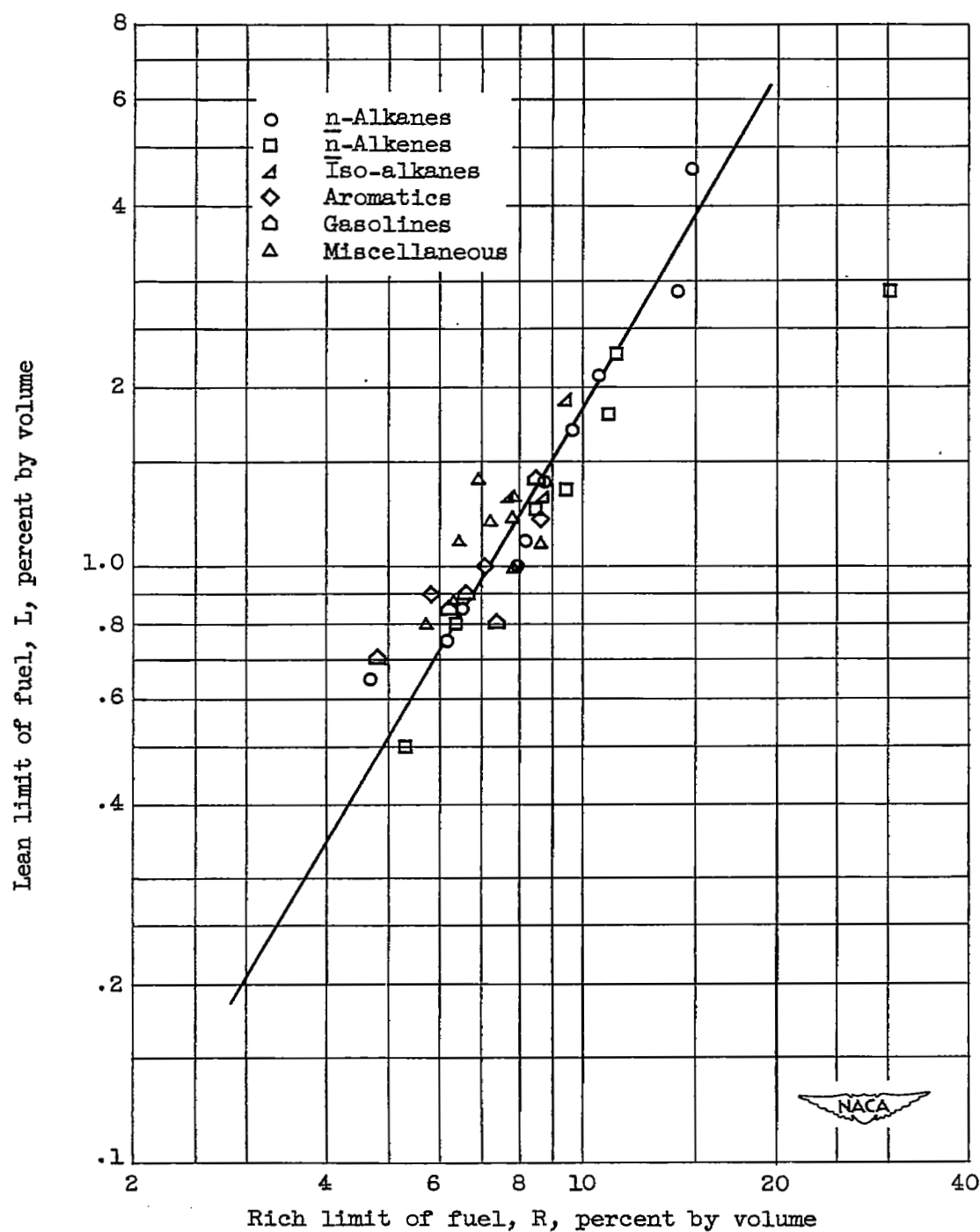Figure 5. - Effect of molecular weight on flammability range of hydrocarbons. $R_a = 143\ W^{-0.70}$.

Figure 6. - Relation between rich and lean flammability limits of hydrocarbon-air mixtures. $R = 7.1\ L^{0.56}$.
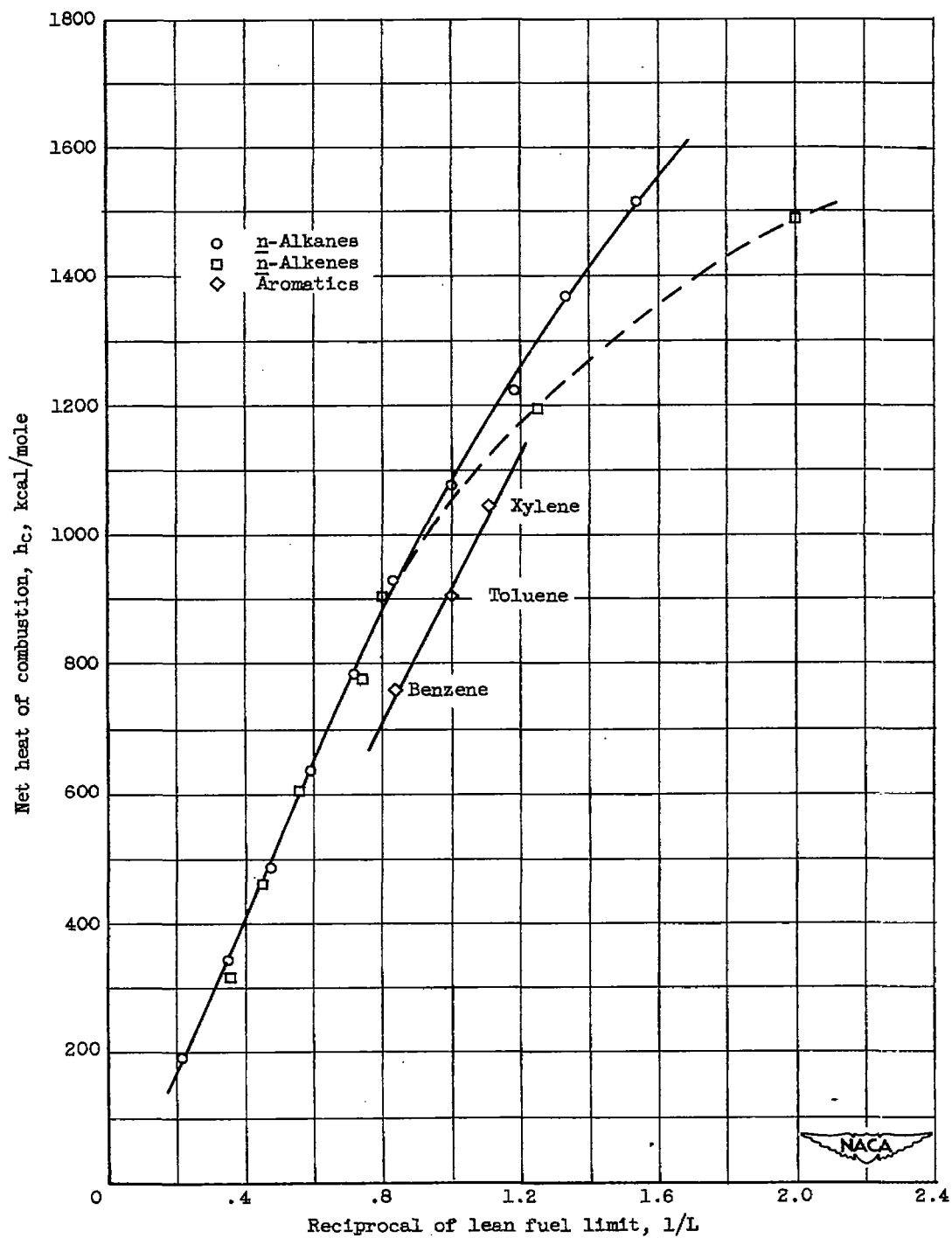
Figure 7. - Correlation of lean limit of hydrocarbon-air mixtures and net molar heat of combustion of fuel.
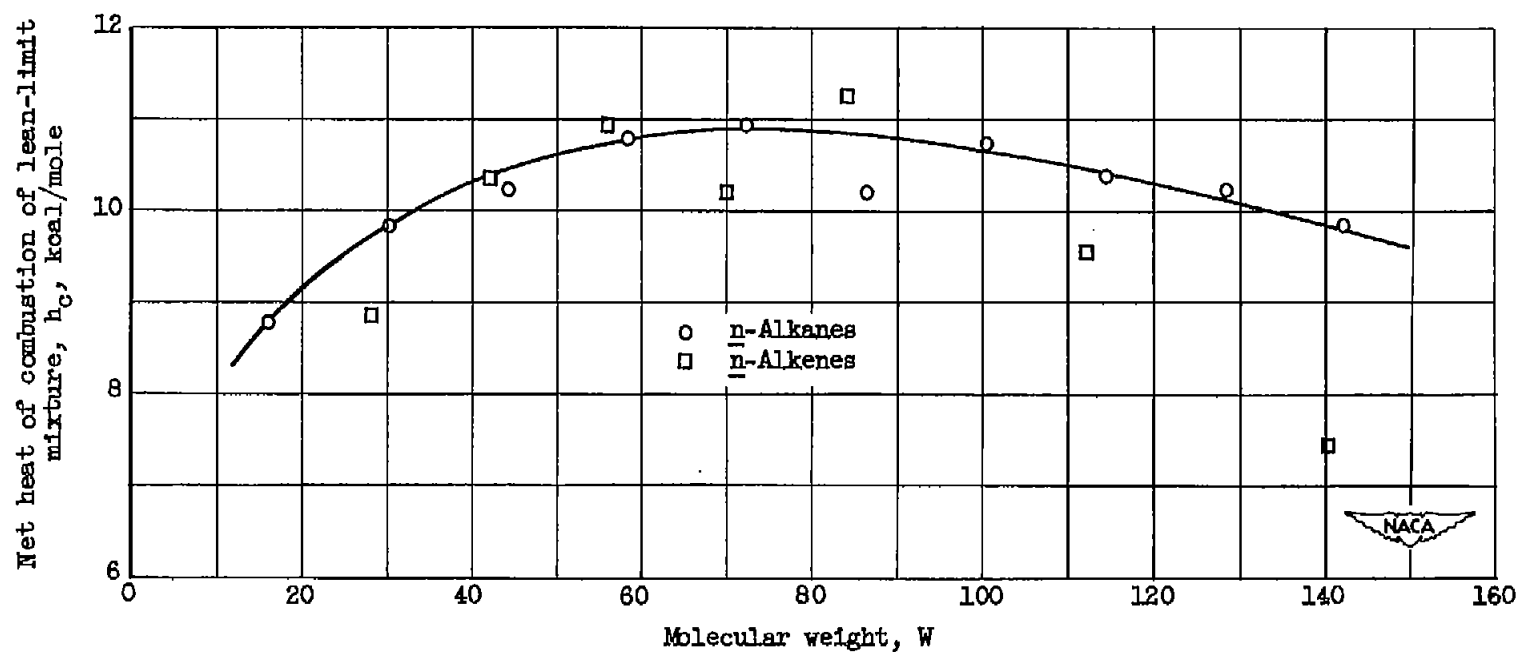
Figure 8. - Effect of molecular weight on heat of combustion of lean-limit mixtures.